Competitive Adsorption at the Air−Water Interface from a Self-Assembling Polymer-Surfactant Mixture

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The relationship between polymer-surfactant aggregation in bulk fluid and adsorption at the air−water interface is investigated in aqueous solutions of sodium dodecyl sulfate (SDS) and Luvitec VA 64 (a random copolymer of vinyl pyrrolidone and vinyl acetate). The polymer exhibits strong interaction with SDS and significant surface activity. The free energy of micellization of SDS in a solution containing 0.1% w/v polymer is reduced by approximately 2.3 RT. The addition of Luvitec VA 64 to a solution of SDS above the critical micelle concentration (*CMC*) results in an increase in surface tension from 40 dyn/cm to 47 dyn/cm. Neutron reflectivity measurements show that the change in surface tension is accompanied by a substantial (greater than 40%) reduction in the volume fraction of SDS at the air−water interface and concomitant adsorption of polymer. The transformation is driven by the decrease in concentration of SDS from the *CMC* to the critical aggregation concentration (*CAC*), consistent with the reduction in free energy of micellization.

Introduction

A mixture of polymer and surfactant is often used in the preparation of colloidal dispersions[1] and emulsions.[2] Typically, the surfactant is needed for reducing interfacial energy for nucleation or shear-induced droplet rupture, whereas the polymer is required for imparting stability against Brownian coagulation, coalescence, Ostwald ripening, or crystal growth.[1] Successful synthesis and stabilization of colloids is dependent on the coexistence of polymer and surfactant at the interface. Although industrial colloidal systems are relatively complex and difficult to analyze, fundamental understanding of the behavior of polymers and surfactants at interfaces may be obtained from investigations at the air−water interface. Initially, such studies were based on surface-tension measurements, as exemplified by the work of Jones[3] and Lange.[4] But more recently, beginning with the work of Chari and Hossain,[5] surface-tension measurements have been complemented by techniques that can selectively examine any one of the surface-active species in a mixture at the interface. A large portion of the work has been enabled by neutron reflectivity in conjunction with isotopic substitution.[6−9] It has been demonstrated that upon addition of surfactant to a solution of the polymer, the more surface-active surfactant will displace the less surface-active polymer from the air−water interface at high enough surfactant concentrations.[6] Furthermore, it has been shown that polymer -surfactant interactions in the bulk fluid may influence the chemical potentials of the adsorbing species.[5,8] More specifically, Jean et al.[8] indicate that although displacement of the polymer will occur in all systems at high surfactant concentrations, the concentration range over which displacement occurs will be modulated by polymer-surfactant interactions.

However, as shown by us in an earlier paper,[5] the effects of polymer -surfactant interaction in the bulk aqueous fluid on adsorption of the amphiphiles at the air−water interface is most evident if polymer is added to a solution of the surfactant that is above the critical micelle concentration (*CMC*). In the system comprising poly (vinylpyrrolidone) (PVP) and sodium dodecyl sulfate (SDS) we showed, using the radiotracer method, that this led to substantial decrease in the amount of surfactant adsorbed at the air−water interface. We also suggested that the partial desorption of surfactant may be accompanied by adsorption of polymer at the interface. *In other words, it might actually be possible for the less surface-active polymer to partially displace the more surface-active surfactant as a consequence of the changes in chemical potential associated with the formation of polymer-surfactant assemblies in bulk water.* This feature is extremely important for providing greater latitude in colloidal formulation. Here we re-visit the phenomenon using Luvitec VA 64 (a random copolymer of vinylpyrrolidone [VP] and vinyl acetate [VA] containing 60 mol % VP and 40 mol % VA) and SDS. We conclusively show for the first time using a combination of neutron reflectivity and surface tension measurements that upon addition of Luvitec to micellar SDS, there is both partial desorption of SDS and adsorption of Luvitec at the air−water interface.

Experimental Section

Materials. A sample of Luvitec VA 64 was obtained from BASF Corporation. The weight average molecular weight (M_w) of the polymer was close to 55 000 with polydispersity (M_w/M_n) of 3.5. The polymer was readily soluble in water at the concentrations used in this study. Sodium dodecyl sulfate was obtained from Eastman Kodak Company and was purified by recrystallizing twice from ethanol. The deuterium-labeled SDS (d-SDS) and deuterium oxide (D_2O) used in neutron reflectivity measurements were obtained from C/D/N Isotopes Inc. and

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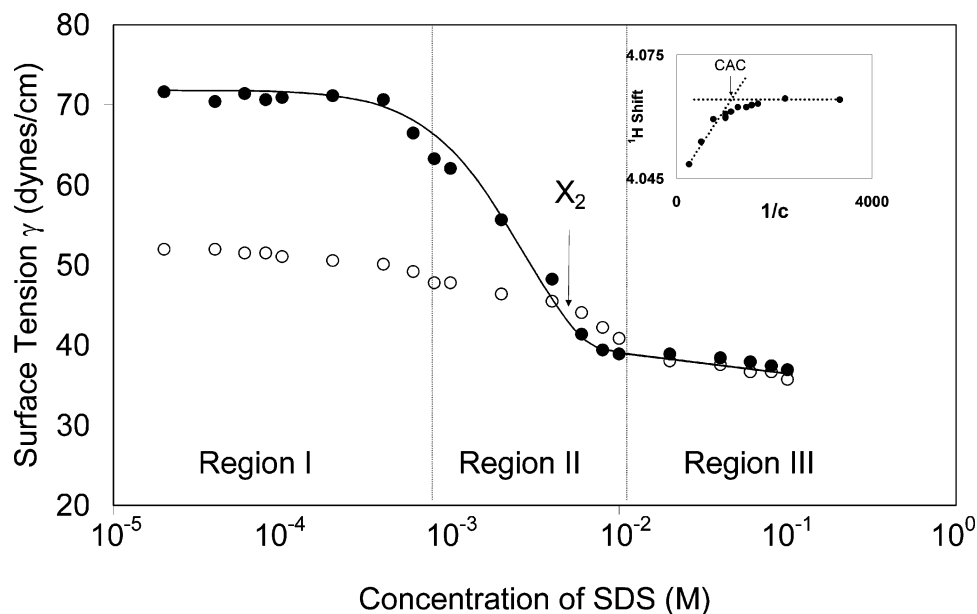† Eastman Kodak Company.

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Figure 1. γ vs log c plot for SDS. Filled circles show the behavior of the surfactant alone, and the empty circles show the behavior in the presence of 0.1% w/v Luvitec VA 64. The latter may be analyzed in terms of three different regions. The inset shows ^{1}H NMR chemical shift (in ppm) of the methylene hydrogens attached to the carbon atom closest to the sulfate headgroup of the SDS molecule as a function of the reciprocal of the surfactant concentration (M^{-1}) in the presence of 0.1% w/v Luvitec VA 64.[10,11] Data obtained in the concentration range 0.3mM to 4mM confirm a CAC close to 0.8mM. Details of the NMR experiment along with other experimental results on the interaction of Luvitec VA 64 with surfactants will be presented in a forthcoming paper.[12]

Cambridge Isotope Laboratories, Inc., respectively. All solutions were prepared using deionized distilled water.

Methods. *(1) Surface Tension.* The surface tension at the air−water interface was determined by the Wilhelmy plate technique. A carefully cut strip of filter paper (analytical paper no. 410 from Schleicher and Schuell, Inc.) that was soaked overnight in deionized distilled water was used as the sensor or "plate" and the force was measured by a Cahn C-32 micro-balance. The values were recorded after equilibrium had been attained. All measurements were made at ambient temperature, 21 ± 0.5 °C.

(2) Neutron Reflectivity. Neutron reflectivity measurements were performed at the NG7 horizontal reflectometer of the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. The sample was placed in a Langmuir trough made of Teflon. The neutron beam was reflected off the surface of the liquid in the trough and the reflected intensity was measured using a position-sensitive detector. The reflectivity was determined as a function of the scattering vector $Q_z = (4\pi/\lambda)\sin\theta$, where θ is the incident angle and λ is the wavelength. Once again all measurements were made at ambient temperature, 21 ± 0.5 °C.

Results and Discussion

Figure 1 shows a variation in the surface tensions of solutions of SDS in water containing 0.1% w/v Luvitec VA 64. The results are qualitatively similar to what has been observed with poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP). At very low levels of SDS (region I), the surfactant does not cause appreciable lowering of surface tension; the main effect here is due to adsorption of polymer at the air−water interface. The polymer displays significant surface activity. One observes a reduction of almost 20 dyn/cm compared to 10 dyn/cm for PVP of similar concentration and M_w.[4,5] There is indication of a second plateau (region II) corresponding to a surface tension of about 47 dyn/cm beginning at an SDS concentration of about 0.8 mM, suggesting formation of polymer-surfactant assemblies

in bulk water. The surfactant monomer concentration and surface tension change only slightly until all available polymer in the bulk fluid is fully saturated with the surfactant (X_2 in Figure 1). Beyond this point, the concentration of SDS monomer increases to the critical micelle concentration (*CMC*) and free micelles are formed (region III). While the overall pattern of the curve is similar to that observed for PVP, the onset of polymer-surfactant aggregation or the critical aggregation concentration (*CAC*) is at significantly lower SDS concentration. Based on the data of Lange,[4] the *CAC* of SDS with 0.1% PVP is 3 mM; the *CAC* decreases to 2 mM for PVP concentrations of 0.3% and higher, but even this is considerably greater than what we observe with Luvitec VA 64 at 0.1%. As a first approximation, one may apply the phase separation model for micelle formation[13] to express the foregoing in terms of a reduction in the free energy of micellization

$$-\Delta G = RT \ln \{CMC/CAC\} \qquad (1)$$

where R is the gas constant and T is the absolute temperature. In eq 1 it is assumed that the surfactant may be regarded as a fully dissociated electrolyte and also that the size of the aggregates is relatively large. The magnitude of $-\Delta G$ for micellization of SDS in the presence of 0.1% Luvitec VA 64 is 2.3 RT based on a *CMC* of 8 mM, whereas with PVP at the same concentration, it is close to 1 RT. It is also possible to determine from Figure 1 a binding ratio or the amount of surfactant bound to unit weight of polymer when the coils are fully clothed with surfactant micelles. The latter is given by $(X_2 - CAC)/C_p$ where C_p is the concentration of polymer. For Luvitec VA 64, it works out to 3.2 mM SDS/g of polymer, whereas for PVP it is 1.5 mM/g. The analysis shows that introduction of the VA moiety in Luvitec VA 64 results in a macromolecule with much higher surface activity and greater propensity to interact with SDS compared to the homopolymer PVP.

Figure 2 shows surface tension of solutions of Luvitec VA 64 in the absence of SDS over the range of concentrations to
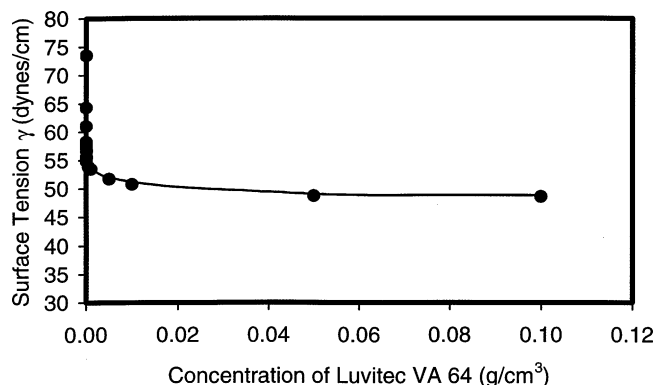
Figure 2. Change in surface tension at the air−water interface as a function of the concentration of Luvitec VA 64 in the bulk aqueous fluid.
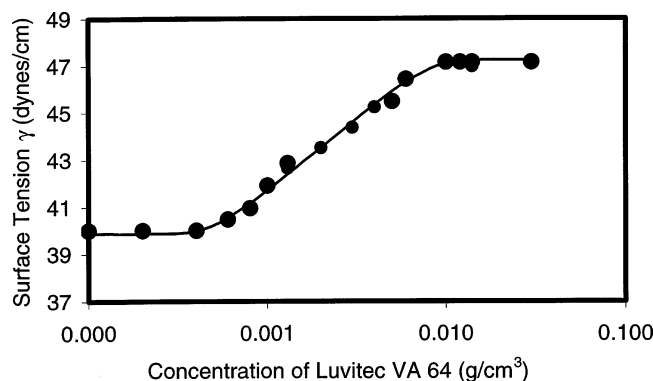

Figure 3. Variation in surface tension at the air−water interface upon addition of Luvitec VA 64 to a micellar (10mM) solution of SDS.

be used in this work. The behavior appears consistent with the theory of Bouchand and Daoud.[14] There is a sharp drop in surface tension at very low concentrations of polymer followed by a "plateau regime" where the surface is saturated with polymer and the surface tension remains relatively constant at about 50 dyn/cm. This should be contrasted with the surface tension of solutions of SDS above the *CMC* (see Figure 1). The latter is close to 40 dyn/cm. Therefore, if one starts with a solution of SDS above the *CMC* and adds polymer to it, one should not normally expect the comparatively less surface-active polymer to displace SDS from a fully packed monolayer at the air−water interface.

Figure 3 shows results of adding increasing amounts of Luvitec VA 64 to a solution of SDS that is above the *CMC*. Here, one observes an increase in surface tension. When polymer is added to a micellar solution of SDS (micelles in equilibrium with monomer), the polymer interacts with the surfactant in bulk water to form self-assembled polymer-surfactant aggregates. Since the free energy of formation of polymer-bound micelles is lower, if sufficient polymer is added, all free micelles are converted to polymer-bound micelles, and the concentration (or activity) of SDS monomer (now in equilibrium with polymer-surfactant aggregates) is reduced from the *CMC* to the *CAC* (i.e., from 8 mM to 0.8 mM in this case).[5,15] It is important to note that the value of surface tension in the upper plateau of Figure 3 is almost identical to that in region II of Figure 1 below X_2, indicating similar composition at the interface in the two cases. As a first approximation, we may express the adsorbed amount of SDS in the presence of polymer as[16]

$$\Gamma = \Gamma_0 + \delta + \ldots\ldots \quad (2)$$

where Γ_0 is the adsorption corresponding to a given chemical potential of surfactant in the bulk fluid in the absence of polymer-surfactant interactions at the interface and δ is a higher-order term representing polymer-surfactant interactions. In other words, the modification of surfactant adsorption by polymer-surfactant interactions is treated as a perturbation of the adsorption of surfactant in the absence of such interactions. If we assume (tentatively) that polymer-surfactant interactions at the interface are weak at bulk concentrations of the order of the *CAC*, we have $\Gamma \approx \Gamma_0$. Therefore, the change in the adsorption of SDS at the air−water interface corresponding to the addition of Luvitec VA 64 to a micellar solution of SDS in Figure 3 may be approximated by application of the Gibbs adsorption equation[17]

$$\Gamma = (-1/2RT) \, (d\gamma/d\ln c) \quad (3)$$

to the γ versus log(c) plot for *SDS in the absence of polymer* in Figure 1 for a decrease in the concentration of bulk *SDS* from the *CMC* to the *CAC*. The analysis suggests a decrease in the surface excess Γ of SDS from about 2.8×10^{-10} mol/cm^2 for the saturated monolayer[18] to about 1.5×10^{-10} mol/cm^2 at the *CAC*. We might also expect the surface tension to increase from about 40 dyn/cm to about 65 dyn/ cm. However, the surface tension at the upper plateau in Figure 3 is only about 47 dyn/ cm. This strongly indicates both desorption of surfactant *and* adsorption of polymer at the interface. In other words, the less surface-active polymer may, in fact, displace the more surface-active SDS at the interface because of a reduction in the SDS monomer concentration from the *CMC* to the *CAC*. These findings are now investigated in more detail by neutron reflectivity.

As stated in the Introduction, neutron reflectivity allows one to examine selectively either the polymer or the surfactant at the air−water interface. We compare the behavior of 10 mM d-SDS with 10 mM d-SDS in the presence of 2% w/v Luvitec VA 64 under three different conditions, based on the scattering length density (*SLD*) of the medium. The surfactant and polymer concentrations correspond to the lower and upper plateau of the curve in Figure 3. In the first instance (Figure 4(a)), we use a mixture of 28% D$_2$O and 72% H$_2$O (*SLD* = 1.42×10^{-6} Å^{-2}) to match the scattering length density of the medium to that of Luvitec VA 64. In the second case (Figure 4(b)), the scattering length density of the medium is matched to that of the surfactant; the *SLD* of pure D$_2$O (6.36×10^{-6} Å^{-2}) is very close to that of d-SDS. In the last instance, pure H$_2$O (*SLD* of -0.56×10^{-6} Å^{-2}) is used as the bulk liquid (Figure 4(c)). In each case, reflectivity is plotted as a function of momentum transfer normal to the surface, Q_z (Å^{-1}). The solid lines represent the best fit to the experimental data and the corresponding scattering length density profiles are shown in the inset. It is evident from Figures 4(a) and 4(c) that the reflectivity is significantly reduced upon addition of polymer. Analysis of the data in Figure 4(a) shows that the *SLD* of the adsorption layer decreases from $(6.5 \pm 0.3) \times 10^{-6}$ Å^{-2} for the surfactant alone to $(4.2 \pm 0.3) \times 10^{-6}$ Å^{-2} on addition of polymer. Furthermore, the thickness of the adsorption layer is reduced from 12.8 ± 0.5 to 11.0 ± 0.5 Å. In other words, there is both a substantial reduction in the amount of d-SDS at the air−water interface as well as a change in its conformation; the hydrophobic tails of the adsorbed surfactant molecules are more slanted and the distance between adsorbed molecules is increased in the presence of the polymer. The experimentally determined *SLD* of the d-SDS monolayer at 10 mM is close to that of pure d-SDS, suggesting that the adsorption layer in this case is almost
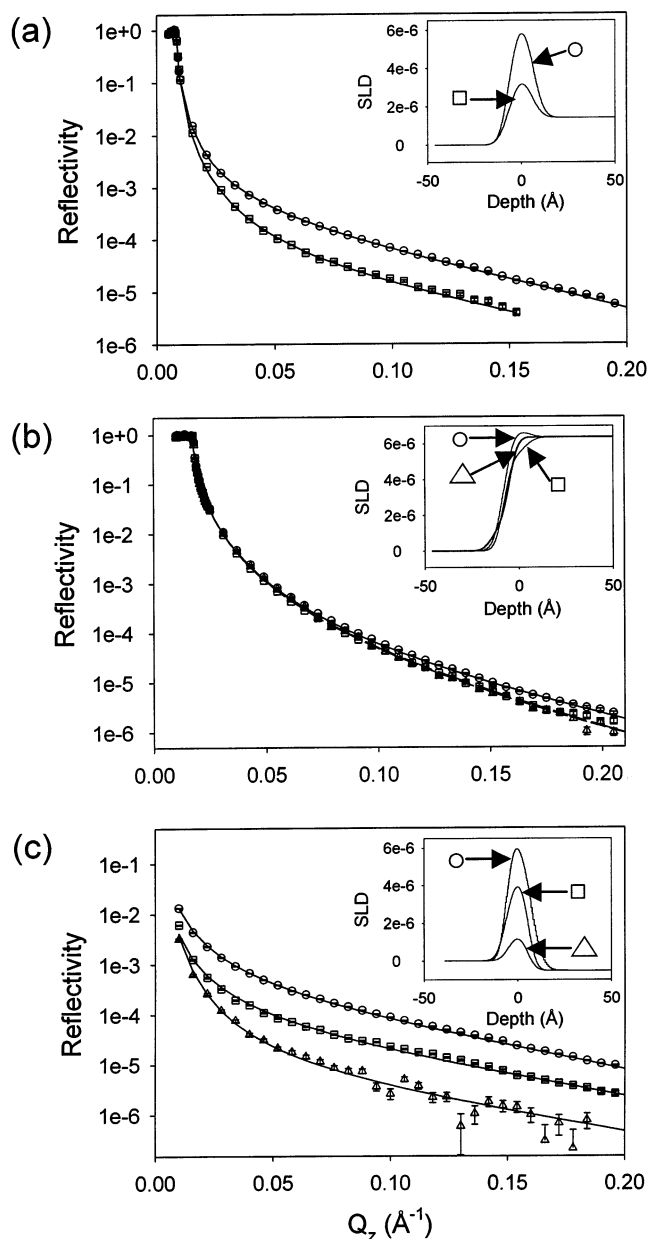
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Figure 4. Neutron reflectivity at the air−water interface versus Q_z for solutions of d-SDS alone, d-SDS in the presence of polymer, and polymer alone in different media: (a) a mixture of 28% D_2O and 72% H_2O with *SLD* of 1.42×10^{-6} Å^{-2}, (b) pure D_2O with *SLD* of 6.36×10^{-6} Å^{-2}, and (c) pure H_2O with *SLD* of -0.56×10^{-6} Å^{-2}. In each case symbol ○ refers to a solution of 10mM d-SDS, □ refers to a solution of 10mM d-SDS with 2% w/v Luvitec VA 64, and △ refers to a solution of 2% w/v Luvitec VA 64. The solid lines represent the best fit to the experimental data, and the corresponding *SLD* profiles are shown in the inset.

entirely composed of d-SDS. The volume fraction of d-SDS in the adsorption layer on addition of polymer may be calculated from the relationship

$$\Sigma \, SLD_i \, \phi_i = SLD_{mix} \qquad (4)$$

where SLD_i is the scattering length density of the ith component in the adsorption layer, ϕ_i is its volume fraction, and SLD_{mix} is the experimentally determined scattering length density for the mixed layer. In this case, the adsorption layer is composed of d-SDS of scattering length density $(6.5 \pm 0.3) \times 10^{-6}$ Å^{-2} and the bulk liquid or medium of scattering length density $1.42 \times$
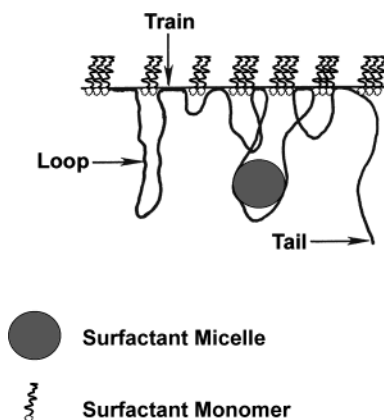

Figure 5. Model of the adsorbed layer in the coexistence regime.

10^{-6} Å^{-2}. The *SLD* of the medium here is the same as the SLD of Luvitec VA 64. The latter is obtained from an analysis of the reflectivity of the polymer alone in water in Figure 4(c). Based on eq 4, the volume fraction of d-SDS is reduced to 0.45 upon addition of Luvitec VA 64, a result that is consistent with the analysis based on surface tension.

The results of Figure 4(b) refer to a medium of pure D_2O, the *SLD* of which is nearly the same as that of d-SDS. The reflectivity is reduced slightly when polymer is added to a monolayer of surfactant. It is interesting to note that the reflectivity profile upon addition of 2% polymer to 10 mM d-SDS in D_2O is almost the same as that obtained with polymer alone in D_2O. It is clear that the addition of Luvitec VA 64 to a micellar solution of d-SDS results in adsorption of the polymer at the air−water interface. Furthermore, the extent of adsorption is similar to that observed in the absence of surfactant. The results confirm our earlier hypothesis that it is possible to achieve coexistence of polymer and surfactant in "soluble" monolayers at the air−water interface, either by the addition of surfactant to an adsorbed polymer monolayer or by the addition of polymer to an adsorbed surfactant monolayer. The latter is enabled by the formation of polymer-surfactant assemblies in the bulk aqueous fluid with which the interface is in thermodynamic equilibrium. Finally, it is clear from Figure 4(c) that the polymer causes only *partial displacement* of the adsorbed surfactant in the transformation from region III to region II. Since the conformation of adsorbed polymer may be expected to be in the form of trains and loops,[19] a significant fraction of the surfactant monolayer can still be accommodated at the surface.[20] If the polymer coil is sufficiently large, it is also possible for spherical micelles to be attached to the loops. A model of the adsorbed layer in the coexistence regime is shown in Figure 5.

Conclusions

In summary, we have studied the influence of polymer-surfactant assembly in the bulk aqueous fluid on adsorption of the species at the air−water interface. We show that if polymer is added to a solution of surfactant that is above the *CMC* and in equilibrium with a fully packed monolayer at the interface, the formation of self-assembled aggregates in the bulk fluid may cause substantial reduction in the chemical potential of the surfactant enabling partial displacement of the adsorbed surfactant by the polymer. We expect the results of this study to be generally applicable in the analysis of more complex systems such as those involving oil−water or particle−water interfaces.

References and Notes

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